

Redox Modification of a Ferrocenylimine Ligands for Iron III-CrCl₂ Catalysis in Ethylene Polymerization

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Abstract: This study explores the redox modification of ferrocenylimines using iodine to develop a novel Iron III-CrCl₂-based catalyst. This catalyst demonstrates exceptional activity in ethylene polymerization under mild conditions, achieving 2.6 tons of polyethylene per mol of catalyst per hour. Electrochemical studies reveal unexpected modifications to the ligand structure, diverging from simple reversible redox processes. These findings open new avenues for designing advanced polymerization catalysts with enhanced efficiency.

Keywords: ethylene polymerization, redox active ligand, ferrocenylimine, Iron III-CrCl₂, catalysis

During the past decade, olefin polymerizations using single-site late transition metal catalysts have attracted considerable attention for both academic and research laboratories. The design of new ligands remains a focal point of intensive research. The goal is the modulation of the steric hindrance and more particularly of the electrophilicity of late metal centers [1], [2]. A first approach is based on the combination of different N, O or P chelating atoms and on their relative positions. Following the metallocene series, α -diimine Brookhart catalysts and all related systems or P-O SHOP type catalysts are some of the representative examples to describe this first approach for olefin activation [3], [4].

Switchable catalysis [5] is particularly attractive for modulating catalytic activity through various stimuli. For instance, by cation exchange for ethylene/acrylate copolymerization [6] or by redox modification of the ligand unit for ruthenium olefin cross metathesis (CM) [7] or acyclic diene metathesis (ADMET). [8].

Furthermore, it was demonstrated that the use of redox-active ligands could be applied to tune the electron-richness of the ligand and the bound metal center. Several examples have shown that redox-active ligands showing stable and reversible oxidation states can affect the catalytic activity by several orders of magnitude, depending on whether the reduced form or oxidized form of the ligand is involved [9]. Ferrocenyl ligands have been extensively described [10] and represented an ideal class of redox active ligands for this study. However, in previous examples [9], [10], the redox switch is only based on the reduced versus oxidized form of the ferrocenyl unit, without any modification of the structure of the ligand itself.

The study aims to develop and analyze a novel catalyst system for ethylene polymerization, leveraging redox-active ferrocenylimines and CrCl₂ to achieve high efficiency and selectivity. The ferrocenylimines **1-3** were synthesized by condensation of formylferrocene and the primary amines benzylamine, furfurylamine and aminomethylpyridine respectively (Figure 1). NMR spectroscopy data are consistent with the proposed structures. [11], [12], [13]

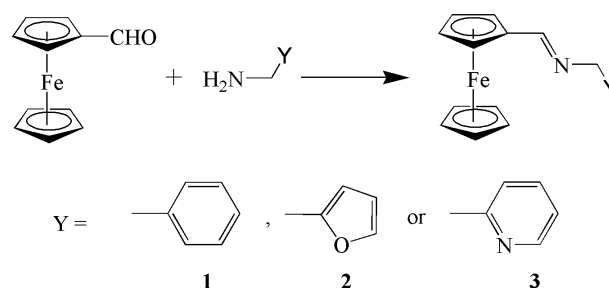


Figure 1: Synthesis of ferrocenylimine ligands **1-3**.

Cyclic voltammetry studies of these ligands were carried out in acetonitrile using tetra-n-butylammonium hexafluorophosphate as the electrolyte, saturated calomel electrode (SCE) as the reference electrode, glassy carbon as the working electrode and platinum as the auxiliary electrode with a scan rate at 100mV.s⁻¹. In all cases, we observed the reversible one electron process for the Fe^{II}-Fe^{III} redox couple of the ferrocene centre (Figure 2). The nature of the Y groups did not influence the redox properties of the ligands as the presence of the methylene moiety between Y and the imine part interrupts the electronic communication between Y and the ferrocenyl part. However, for all ligands the Fe^{II}/Fe^{III} redox systems shift to a higher positive potential (550mV Vs 430 mV) than the ferrocene reference, indicating the electrowithdrawing effect of the imino functionality [14], [15]. Cyclic voltammetry at 1.5V reveals an irreversible transformation of ligands **1-3**.

These studies help us to select the redox window to transform the ligand **1-3** into corresponding ferricinium ligands **1⁺-3⁺** without affecting the rest of the ligands. In order to avoid the use of large excess of electrolyte, generally involved in electrochemical preparative methods, we have focused on the use of chemical redox agents for the selective and clean oxidation of ligands **1-3** into **1⁺-3⁺**.

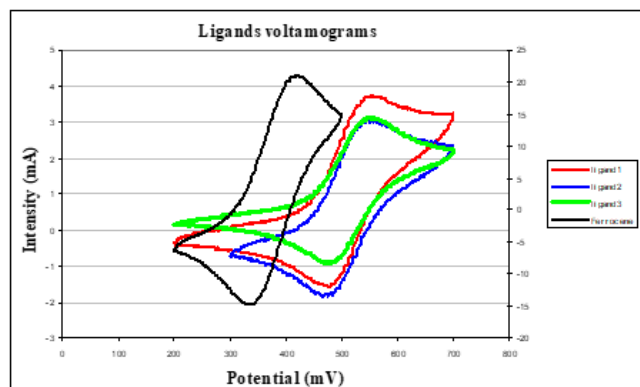


Figure 2: Electrochemical response of redox active ligands **1-3** by cyclic voltammetry

Iodine I_2 was selected to oxidize ligands **1-3** because it has a suitable oxidant ($E_{1/2}=636\text{mV/SCE}$) for the ferrocenyl unit without affecting the integrity of ligands **1-3**, i.e. oxidation process under 1.5V [16]. The excess of I_2 is also easily removable with diethyl ether washing when the ferricinium ligands 1^+-3^+ are insoluble in diethyl ether. Reaction of one equivalent of ligand **1-3** with one equivalent of iodine in acetonitrile resulted in a color change from orange-brown to dark blue solutions. After evaporation of solvent and washing with diethyl ether until colorless filtrate, the dark blue solids 1^+-3^+ were obtained.

a) Complexation and catalysis studies:

After the complexation of neutral ligands **1-3** with CrCl_2 in THF for 2 hours, the solvent was evaporated. The corresponding solutions were directly involved in the polymerization of ethylene in toluene with 1000 equivalents of MAO, 15bars of C_2H_4 at 35°C . After 1 hour the reactor was opened after pressure removal and acidified methanol was added. After filtration and washing, the polyethylene was dried in a vacuum overnight. The results are reported in table 1.

Table 1: Activities of combinations **1-3**/ CrCl_2 and 1^+-3^+ / CrCl_2 for ethylene polymerization

	Ligand 1	Ligand 2	Ligand 3
Neutral ligand	0	13	90
Oxidized ligand	90	67	1200

Activities are in kg (PE)/mol(catalyst)/h. Polymerization conditions: 15bars, 35°C , 1h, 60mL of toluene

CrCl_2 alone without any ligands was practically inactive. The combinations of ligands **1-2** and CrCl_2 were inactive. Only the pyridine unit containing ligand **3** showed a moderate activity when associated with CrCl_2 (90kgPE/molCr/h). The complexation of CrCl_2 via the imino functionalities only (i.e. no interaction of the Y group) seems unreliable, as it should give similar results for polymerization activity for all catalyst based on ligands **1-3**.

Using the same conditions for the complexation reaction and the polymerization step, the corresponding catalysts based on oxidized ligands 1^+-3^+ were clearly more active, with the greatest activity observed once again with the ligand containing the pyridine part (1200kgPE/molCr/h). The strong increase in activity observed with the oxidized

version of ligands could be explained by a more electrophilic chromium center, and hence a faster rate of ethylene insertion, induced by the electron-withdrawing effect of the ferrocenium unit.

b) Optimization of catalytic conditions with the best system CrCl_2 / ligand 3^+

Different temperature and pressure polymerization conditions were investigated for the new redox active $3^+/\text{CrCl}_2$ system (Table 2).

- Impact of temperature: At room temperature a strong decrease of activity (600kg PE/molCr/h), using 15 bars of C_2H_4 , was observed by comparison with polymerization at 35°C (1200kg PE/molCr/h). However, the impact of temperature at 15 bars was not observed at 24 bars and 45 bars as similar results were obtained at 25°C and 35°C . (Table 2). Additional experiments at higher or lower temperature, with 24 bars were performed. However, higher temperatures strongly reduced the activity at this pressure (827 kg (PE)/mol(catalyst)/h at 55°C and 278 kg (PE)/mol(catalyst)/h at 85°C). At 0°C and 24 bars, correct activity was measured (1120kg of ethylene were consumed) but only 320kg of PE were obtained. This indicated that the high selectivity for the polymerization was lost and that oligomerization occurred at 0°C .
- Impact of pressure: For both temperature conditions, i.e. 25°C and 35°C , the pressure clearly induced a strong effect with an increase of activity from 15 to 45 bars. A very active polymerization catalytic system was obtained with 2.6 tons of PE per mol of $3^+/\text{CrCl}_2$ combination per hour with a total selectivity for the polymerization process versus an oligomerization process.

Table 2: Activities of system CrCl_2 / ligand 3^+ for ethylene polymerization

T/P	15 bars	24 bars	45 bars
25°C	600	1966	2400
35°C	1200	1800	2600

Activities are in kg (PE)/mol(catalyst)/h. Polymerization conditions: 1h, 60mL of toluene

c) Electrochemical study for $3^+/\text{CrCl}_2$ system

Until now, no satisfactory single crystal for X-Ray structure determination of LCrCl_2 and L^+CrCl_2 complexes has been obtained. Thus, only a hypothesis of potential coordination can be proposed at the moment. The coordination with only the pyridinium unit with the CrCl_2 centre should not present a difference between the neutral and oxidized ligands due to the presence of the methylene part. It should be noted that even if the methylene group interrupts the electronic communication between the ferricinium unit and the Y group, the presence of the pyridine Y moiety is essential for a high activity (comparison 2^+ and 3^+). In order to elucidate the structure of the ligand 3^+ and $3^+/\text{CrCl}_2$ complexe, we performed cyclic voltammetry studies.

The figure 3 reports the cyclic voltammetry of the complex $3^+/\text{CrCl}_2$ in acetonitrile using tetra-n-butylammonium hexafluorophosphate as the electrolyte, saturated calomel

electrode (SCE) as the reference electrode, glassy carbon as the working electrode and platinum as the auxiliary electrode with a scan rate at $100\text{mV}\cdot\text{s}^{-1}$. The 80 mv shift between $3^+/\text{CrCl}_2$ (blue curve) and the oxidized ligand 3^+ (pink curve) is consistent with the electro-withdrawing effect of the complexation with the Cr center. However, the comparison with the neutral ligand **3** (green curve in Figure 2) and the corresponding oxidized ligand 3^+ indicates that a new ligand is produced because the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox system is at 250 mv (pink curve figure 3) for ligand 3^+ and not at 550 mv as expected (green curve figure 2).

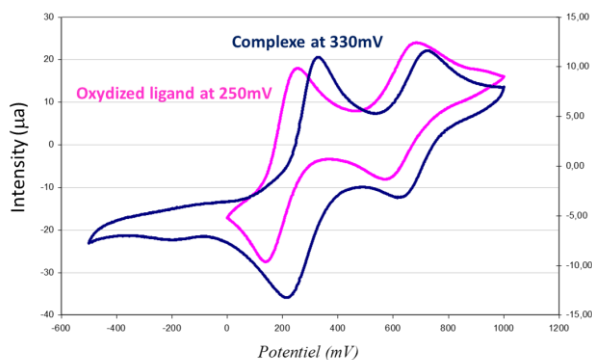


Figure 3: Cyclic voltammetry of oxidized ligand 3^+ (Pink) and after its complexation with CrCl_2 (Blue).

This clearly indicates that the iodine not just oxidized the ferrocene unit but also induced a modification of ligand **3** itself. The shift from 550 mv for the initial ligand to 250 mv for the new system after oxidation by iodine indicates a richer ferrocenyl unit than the expected ferrocenyylimine. To be sure that the Fc unit in the complex $3^+/\text{CrCl}_2$ is at oxidation state Fe III, we have performed a linear sweep voltammetry at a rotating glassy carbon disk RDE [17]. Rotating speed 1000 rpm; Sweep rate 20 mV/s; reference electrode ECS in acetonitrile. As shown in figure 4, at potential negative to the equilibrium state (Blue curve), we have a signal corresponding to the reduction of Fe^{3+} in Fe^{2+} (Pink curve). In presence of Fe^{2+} , the signal should start after the equilibrium state and should show a positive intensity. The same behavior was found for the free oxidized ligand 3^+ .

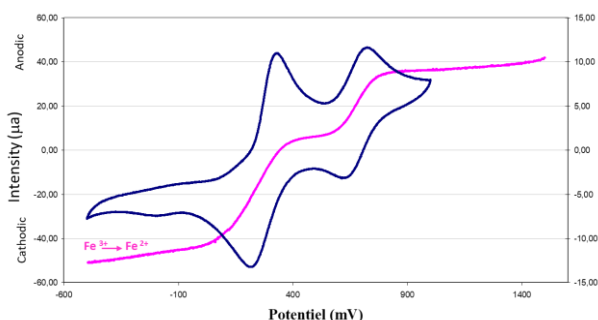


Figure 4: Linear sweep voltammetry at rotating glassy carbon disk RDE for the complex $3^+/\text{CrCl}_2$ (Pink)

This led us to conclude that after oxidation of **3** by iodine and complexation with CrCl_2 , we always have a ferricinium unit but into a different catalytic system than the simple reversible redox switching of ferrocenyylimine ligand ferrocenyylimine 3^+ . This study is significant as it introduces

a new catalytic system for ethylene polymerization, which could potentially revolutionize polymer production by offering higher efficiency and selectivity under mild conditions.

All polymers obtained during this study were insoluble in hot trichlorobenzene indicative of very high molecular weight.

In conclusion, this preliminary study indicated that redox active ligands could be applied to strongly raise the activity of a catalytic system for ethylene polymerization. A very active polymerization catalytic system was obtained with 2.6 tons of PE per mol of $3^+/\text{CrCl}_2$ combination per hour with a total selectivity for the polymerization process versus an oligomerization process. However, it should be noted that the oxidation process can involve not only the ferrocenyl unit but also could give a totally different catalytic system than the simple reversible redox switching of ferrocenyylimine ligand.

This study demonstrates the potential of redox-active ferrocenyylimines in developing highly efficient polymerization catalysts. Future research should aim to elucidate the structural modifications induced during oxidation and expand the applicability of this catalytic system to other polymerization processes.

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